

## Hydrofracturing, fluid flow, and rhythmic precipitation of carbonates in marble: An example of orbicular marble

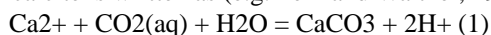
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The Hirao Limestone at Hirao-dai, Kita-kyushu City, is considered to be a Paleozoic limestone bed metamorphosed by Cretaceous granites, and now consists of completely re-crystallized limestone ( marble ) with little fossil evidence (Fukuyama et al., 2004, 2006; Urata, 2009 ). We newly found a peculiar zone with orbicular structure in the marble, and refer it as an orbicular marble hereafter. The orbicular marble occurs as a narrow zone of about 1 meter width, extending about 20m straight from north to south. In parallel to the zone occurs several veins of dolomite with various width ranging from several millimeters to 5 centimeters in the marble. The zone contains a lot of angular fragments of marble, several centimeters to 10 centimeters in size, surrounded by alternating thin layers of dolomite and calcite. The resulting structure looks concentric orbicules. The number of alternating layers is typically more than 10. The thickness of each thin layer is variable, ranging from 1 mm to 6 mm. The interstices between orbicular marbles are filled with dolomite. The angular fragments sometimes show jig-saw puzzled structure with neither clay nor fine-grained crushed materials between the fragments. The contact between the zone of orbicular marble and the country rock ( massive marble ) is sharp and shows no obvious displacement.

The occurrence of the orbicular marble zone suggests that the zone was originated as a tensile fracture caused by hydrofracturing and that fluid flew through the fractured zone and precipitated dolomite and calcite around the fragments formed by fracturing. The absence of clay and gouge strongly supports hydrofracturing rather than faulting for the origin of tensile fracture.

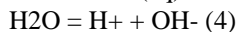
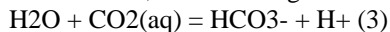
We will present here a qualitative model to explain alternate precipitation of dolomite and calcite. The precipitation reaction of calcite is written as (e.g. Fein and Walther, 1989)



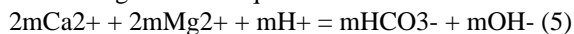
Assuming similar reaction for dolomite, we get



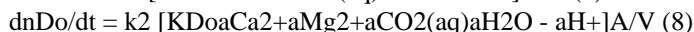
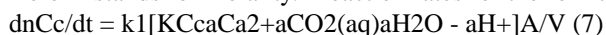
In the fluid, the following two reactions occur together with the above two reactions(Fein and Walther, 1989):



The charge balance equation holds for these reactions:

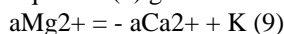


Here m stands for molality. Reaction rates for the formation of calcite and dolomite can be modelled as:

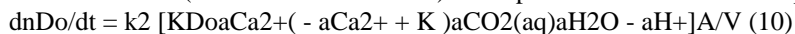


All the reactions are assumed to be 1st order. KCc and KDo represents equilibrium constant for calcite and dolomite, respectively, and k1 and k2 are rate constants. A/V stands for specific area( area / solution volume ). Assuming ideal dilute solution, activity is equal to molality.

Equation (5) gives



We assume  $\text{K} = (\text{aHCO}_3^- + \text{aOH}^- - \text{aH}^+)/2$  is a positive constant. Then equation (8) becomes



Antivity of H<sub>2</sub>O is almost unity in the dilute solution, then qualitative behavior of the solutions can be discussed in an aCa<sup>2+</sup> vs. aH<sup>+</sup> plane under constant aCO<sub>2</sub>(aq), by using nullclines of (7) and (10). The two nullclines intersect at a certain point with positive values of aCa<sup>2+</sup> and aH<sup>+</sup>, which represents an equilibrium point. Precipitation of dolomite and calcite occurs interchangeably while the solution changes its composition around the equilibrium point.

Keywords: periodic precipitation, hydrofracturing, fluid flow, dolomite, calcite, orbicular marble